FOREIGN EXPERIENCE

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USE OF SEQUENTIAL X-RAY FLUORESCENCE ANALYSIS FOR SOLVING ANALYTICAL PROBLEMS IN THE GLASS INDUSTRY

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The capabilities of x-ray spectral instruments for fast analysis of raw materials and glass and ceramics were demonstrated. The range of the content of determinable elements in a sample ranges from 1 ppm to 100%. The measurement time is 10 – 15 sec.

Heightened requirements are currently imposed for solving analytical problems. For this reason, it is impossible to do without a scientifically oriented base where precision chemical analysis of the initial raw material, finished products, and intermediate control ensure the optimum manufacturing process, saving time, rational consumption of raw material and power, decrease the amount of rejects, and increase the yield of finished products with given physicochemical properties. Current methods of analyzing the chemical and phase (structural) compositions of materials are used in different sectors of industry, including in ceramics factories and glassworks.

Thermo Techno, Ltd. proposes the following equipment for fast x-ray spectral analysis (Fig. 1):

the ARL OPTIM'X x-ray spectral instrument for glassworks that found boron-free glass and for manufacturers of ceramic materials and ore concentration combines;

the ARL ADVANT'XP x-ray spectral instrument for glassworks that found borosilicate and electrovacuum glass;

the ARL X'TRA diffractometer for manufacturers of ceramic materials and ore-concentration combines.

The XRF method (method of x-ray spectral analysis), which allows accurately analyzing up to 83 periodic table elements (from B to U), has the following features: different samples are used — solid, liquid, powdered, electrically conducting and nonconducting.

The advantages of XRF analysis are:

effect of one sample;

speed of analysis — several minutes;

simplicity of sample preparation;

high stability and reproducibility of the results, accuracy of the analysis, and wide range of the content of determinable elements — from 1 ppm to 100%.

The analytical parameters and limits of detection of different oxides and elements in glass (recording time of 100 sec; the amount of characteristic photons irradiated in the K_α transition is measured; tube excitation conditions: 50 kW/70 mA). The analytical limits of detecting elements in glass are very small, which indicates the high accuracy of the measurements.

As an example, consider the solution of several analytical problems facing laboratory works in glassworks.

Problem 1. Accurate determination of the oxide content in glass. An ARL ADVANT'XP spectrometer was used to calculate the limits of detection and convergence of the re-

Fig. 1. X-ray spectrometer sand diffractometer from Thermo Fisher Scientifics.

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TABLE 1

Oxide, element	Crystal	Detector	Detection limit, ppm (10^{-4}%)
Na_2O	AX-06	FPC flow-proportional	Unlimited
MgO	AX-06	Same	10.3
Al_2O_3	PET	″	2.7
SiO_2	PET	″	Unlimited
Cl	PET	″	3.0
SO_3	PET	″	0.9
K_2O	LiF200	″	1.3
CaO	LiF200	″	Unlimited
TiO_2	LiF200	″	0.8
Fe_2O_3	LiF200	″	1.1
As_2O_3	LiF200	SC scintillation	0.5
SrO	LiF200	Same	1.0
Co_2O_3	LiF200	FPC flow-proportional	0.9
Se	LiF200	Same	1.0

sults of analyzing the glass. The instrument's geometry was optimized for the maximum sensitivity. The instrument was equipped with a 4th generation (4GN) x-ray tube with a rhodium anode and a beryllium end window 75 μm thick. The thin window improves the efficiency of exciting the elements more easily than potassium.

Several samples of sheet glass were measured on the ARL ADVANT'XP spectrometer. The calibration curves were calculated with the intensities obtained for each oxide (element) in standard samples. The content of the elements was measured by the x-ray fluorescence method. The results obtained are compared with the oxide forms of these elements. If several kinds of determinable oxides are present in the sample, then the recalculation is performed for one selected kind. The limits of detection of the basic oxides encountered in sheet glass were calculated with the calibration curves.

The tests for convergence of the results were performed with ten parallel measurements of the samples. The convergence of the results of analyzing the basic oxides in glass (recording time of 10 sec, i.e., total duration of the analysis of 80 sec) is shown in Table 2.

The convergence of the results of analyzing the basic oxides in the glass is reported in Table 3 (total duration of the analysis of 116 sec).

The ARL ADVANT'XP spectrometer can thus be used to obtain the limits of detection of metal oxides in glass at the 1 ppm level, i.e., 10^{-4}%. Very good brief stability is attained even with a short recording time. This indicates that the ARL ADVANT'XP spectrometer can give accurate results in determining the content of basic oxides and coloring reagents in glass.

Problem 2. Accurate determination of the B_2O_3 content in sheet glass. In substitution of alkali oxides by boron oxide, glass with a low TCLE, good thermal stability, and chemical stability is obtained. In addition, the softening point of quartz decreases significantly. The B_2O_3 content can vary from several percent in quartz, aluminosilicate, or lead glass to 30% in glass with low energy losses.

Determination of the B_2O_3 content in glass by titration takes several hours and involves the use of hazardous chemicals. The modern x-ray fluorescence spectrometer reduces the measurement time to several minutes.

A set of six samples was used for quantitative analysis in optimally selected analytical conditions. The data from scanning the characteristic K_α peak of the boron element for determination of angle 2θ, whose values are necessary for plotting the calibration curve (Fig. 3), are shown in Fig. 2. Using the sensitivity (slope) and background level indicated on the curve, the boron detection limit can be calculated (0.04%). The recording time for the element B_2 is 100 sec and the duration of the analysis is 120 sec.

TABLE 2

Measurement	Mass content, %							
	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	Fe_2O_3, 10^{-4}
1	11.35	0.245	2.78	69.97	0.214	1.91	9.97	369
2	11.34	0.250	2.77	69.93	0.213	1.90	9.97	372
3	11.36	0.250	2.77	69.97	0.211	1.91	9.96	373
4	11.35	0.251	2.78	69.93	0.211	1.91	9.98	377
5	11.33	0.252	2.77	69.95	0.210	1.91	9.97	376
6	11.33	0.251	2.77	69.93	0.213	1.90	9.99	370
7	11.35	0.252	2.78	70.00	0.211	1.91	9.97	372
8	11.36	0.249	2.77	69.96	0.214	1.91	9.96	375
9	11.35	0.252	2.78	69.95	0.210	1.91	9.97	374
10	11.35	0.250	2.77	69.99	0.211	1.91	9.98	377
Average value	11.35	0.250	2.77	69.96	0.212	1.91	9.97	374
Degree of difference	0.012	0.0023	0.005	0.029	0.020	0.004	0.009	3

TABLE 3

Measurement	Mass content, %									
	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	Cl, 10^{-4}	K_2O, 10^{-4}	CaO	TiO_2	Fe_2O_3, 10^{-4}
1	13.75	4.13	0.580	71.33	0.388	117	128	9.61	0.017	145
2	13.76	4.15	0.578	71.32	0.390	119	132	9.62	0.017	146
3	13.76	4.15	0.575	71.31	0.391	115	133	9.62	0.016	148
4	13.77	4.16	0.579	71.32	0.390	115	130	9.62	0.017	146
5	13.77	4.15	0.579	71.34	0.388	120	136	9.62	0.017	146
6	13.77	4.15	0.576	71.32	0.389	116	132	9.62	0.017	147
7	13.76	4.15	0.578	71.32	0.385	114	131	9.62	0.016	147
8	13.76	4.15	0.578	71.33	0.388	114	132	9.61	0.017	145
9	13.76	4.15	0.580	71.32	0.386	121	129	9.62	0.018	145
10	13.75	4.14	0.577	71.33	0.383	118	133	9.62	0.017	146
Average value	13.76	4.15	0.578	71.32	0.388	117	132	9.61	0.017	146
Degree of difference	0.009	0.01	0.002	0.007	0.002	2.4	2.4	0.004	0.0005	1
Recording time, sec	20	6	20	20	6	6	6	6	6	20

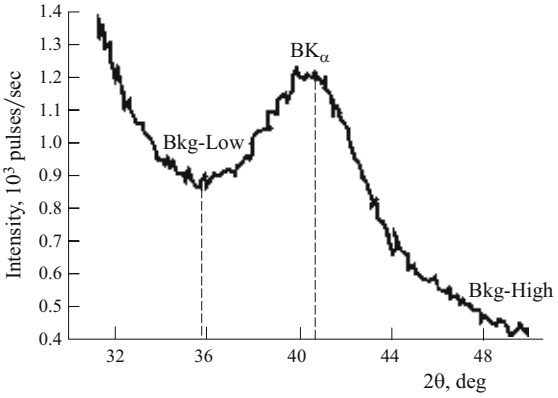

Fig. 2. Data from scanning the K_α peak of boron in glass.

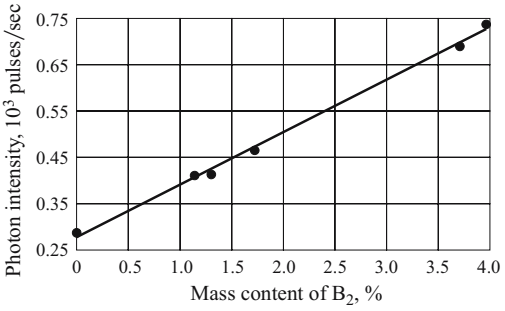

Fig. 3. Calibration curve for determining the boron content in glass.

As a result of introducing the latest developments in the new spectrometer, the detection limits of superlight elements are reduced significantly, which allows improving the analysis of difficult to determine elements. The optimized spectrometer can replace the laborious "wet" chemistry process and accelerate obtaining results.

It should be noted that the x-ray radiation penetrates glass to a depth of 0.15 μm, i.e., only surface boron is analyzed. To improve the analysis, the corresponding quality of preparation of the surface of the glass samples and minimization of contamination are necessary. If the necessary measures are not instituted, the results will not be reliable, since contamination of the surface will prevent emission of x-rays and this radiation will not be recorded by the spectrometer.